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MOLECULAR DYNAMICS SIMULATION ON MAGNESIUM CHLORIDE IN CONCENTRATED SOLAR THERMAL POWER GENERATION SYSTEM

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ABSTRACT

Molten salt is the popular thermal storage material in concentrating solar power system. With the development and utilization of magnesium resources, molten salt containing magnesium has been attracted much attention, but the thermal properties of magnesium chloride over a wide temperature range fail to be well predicted. In present paper, thermal properties and local structure of magnesium chloride are predicted and analyzed by molecular dynamics simulation(MD). This work uses Born-Mayer-Hugging pair potential, which is convinced by a lot of research. In order to well predict thermal conductivity, equilibrium molecular dynamics (EMD) is proposed. Results show that Mg and Cl form the typical tetrahedral structure. Thermal conductivity of $MgCl_2$ increase with increasing temperature. This study helps to build the molten salt database for the application in industrial applications.

Keywords: molecular dynamics simulation, molten salt, magnesium resources, solar thermal power generation, thermal property, local structure

1. INTRODUCTION

Concentrating solar thermal power (CSP) has attracted extensive attention due to its many advantages [1]. In order to overcome the intermittent over time of CSP, thermal energy storage (TES) has been developed in large scale. Molten salt is the suitable material for thermal energy storage due to its good properties[2]. China has abundant magnesium resources, which promotes the wide application of magnesium-containing molten salt in thermal energy storage system.

KCl-$MgCl_2$ has been one potential material in energy issues[3]. Molten salt containing magnesium is the high temperature heat transfer and thermal storage fluid in concentrating solar thermal power systems[4]. Wei et al.[5] developed a ternary chloride salt mixture containing magnesium and measured thermal properties of heat capacity, density and viscosity at high temperature. Li et al.[6] prepared appropriate binary and ternary mixtures with NaCl, KCl, $MgCl_2$, $CaCl_2$, and $ZnCl_2$. They provided experimental and predicted thermophysical properties of 16 selected eutectic binary and ternary molten salts.

According to above studies, it was found that molten salt containing magnesium is the promising potential material in energy issues, especially in CSP system. Therefore, thermal properties of them need to be measured. But data of properties can just be obtained in a narrow temperature range. This paper mainly focuses on theoretical prediction of properties of magnesium chloride with MD method. The properties are calculated in a wide temperature range. This work helps to well predict the thermal properties and structures of molten salt containing magnesium and

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their mixtures. It is also significant to build the molten salt database for the application in industrial applications.

2. NUMERICAL MODEL AND CONDITIONS

2.1 Force field

The potential function is composed of three parts: bonded term, non-bonded term and cross energy term. Since cross energy term has little influence on the overall potential energy, it is ignored in the calculation in this study. The Born-Mayer-Coulomb potential function is adopted for non-bonding terms, as shown in Formula (1).

$$U_{ij} = \frac{q_i q_j}{r_{ij}} + A_{ij} \exp\left(\frac{\sigma_{ij} - r_{ij}}{\rho}\right) - \frac{C_{ij}}{r_{ij}^6} - \frac{D_{ij}}{r_{ij}^8} \quad (1)$$

2.2 Simulation details

The simulations carried out by LAMMPS code consisted of 9000 ions and the amounts of Mg and Cl were allocated as the proportion of 1:2. The Periodic Boundary Condition was adopted to remove side effects. The cutoff distance was set to 13 Å and apply long-range corrections via PPPM solver while the precise was set equal to 1.0×10^{-4}. Newton's equations of motion was solved by Verlet computing method. The time increment was set to 1.0 fs.

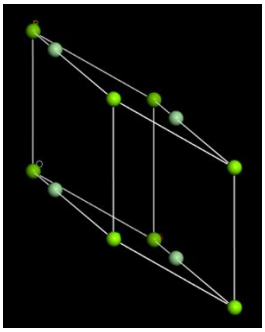


Fig 1 RDF curves of magnesium chloride

2.3 Evaluated properties

2.3.1 Partial Radial Distribution Functions

The local structure of molten alkali chloride is described by Partial radial distribution function (RDF) defined as $g_{\alpha\beta}(r)$ for ion pair of species α and β.

$$g_{\alpha\beta}(r) = \frac{1}{4\pi\rho_\beta r^2}\left[\frac{dN_{\alpha\beta}(r)}{dr}\right] \quad (2)$$

in which ρ_β denotes the number density of species β.

2.3.2 Coordination number

Coordination number ($N_{\alpha\beta}$) denotes the number of β-type ions lying in a sphere of radius r_{min} centered on an α-type ion, where r_{min} is the position of the first peak valley of RDF. $N_{\alpha\beta}$ can be calculated from RDF as follow:

$$N_{\alpha\beta} = 4\pi\rho_\beta \int_0^{r_{\min}} g_{\alpha\beta}(r) r^2 dr \quad (3)$$

The ionic equilibrium distance corresponds to the position of the first maximum of the RDF.

2.3.3 Density

$$\rho = \frac{NM}{V_E N_A} \quad (4)$$

in which N denotes the particle number, M denotes the molar mass, N_A is Avogadro's constant, and V_E is the equilibrium volume of the simulation cell at the given temperature in the NPT ensemble simulations.

2.3.4 Thermal expansion coefficient

The volume expansion coefficient hinges on the change of volume with temperature and is defined as follows

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \quad (5)$$

where V and ρ denote the volume of the simulation box and density at corresponding equilibrated temperature T, respectively.

2.3.5 Thermal Conductivity

The thermal conductivity can be calculated from the time integral of the heat flux auto-correlation function of the material simulation system.

$$\lambda = \frac{V}{3k_B T^2}\int_0^\infty \left\langle J_{q\_\alpha}(0) J_{q\_\alpha}(t)\right\rangle dt \quad (6)$$

where V is the volume of the simulated system, and T is the temperature. A is the heat flux component in Cartesian coordinates, α represents the x, y, and z directions.

2.3.6 Specific heat capacity

Specific heat capacity is the slope of enthalpy versus temperature under constant pressure, and is defined as follows:

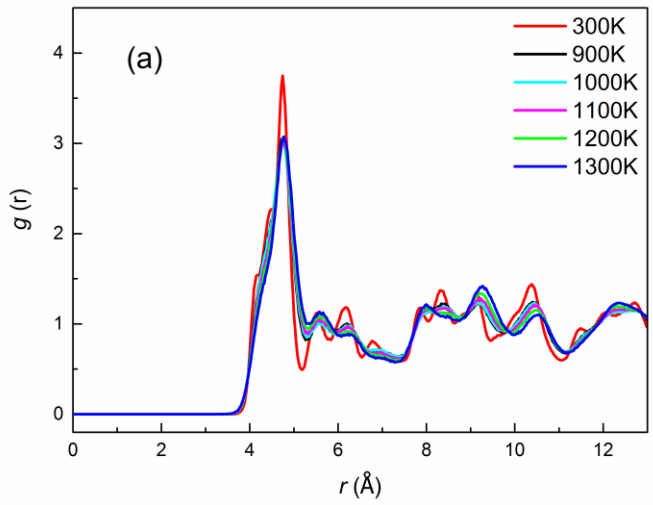
$$C_p = (\frac{\partial H}{\partial T})_P \approx (\frac{\Delta H}{\Delta T})_P \quad (7)$$

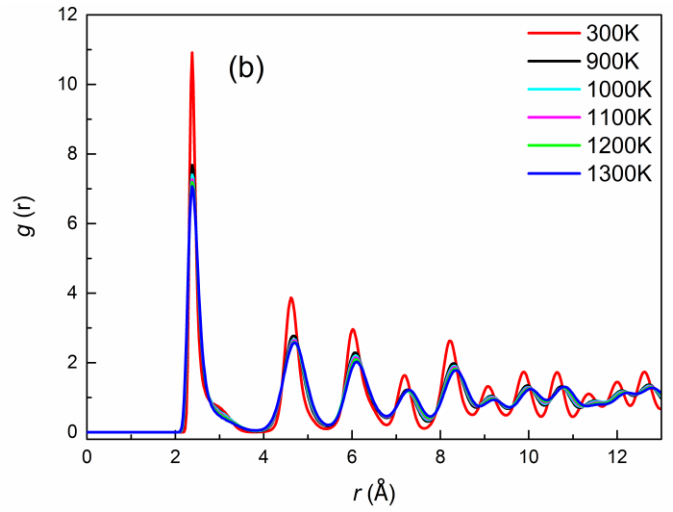
3. RESULTS AND DISCUSSION

3.1 Partial Radial Distribution Functions

In order to study the evolution of the melt structure of $MgCl_2$ molten salt with temperature, the partial radial distribution function and coordination number of the $MgCl_2$ molten salt were simulated.

As Fig.2 shows, the partial radial distribution function(RDF) of molten $MgCl_2$ has several undulation peaks in a short distance. As the distance increases, the peak weakens and slowly fluctuates around 1. This reveals the short-range order and long-range disordered structure of molten salt.





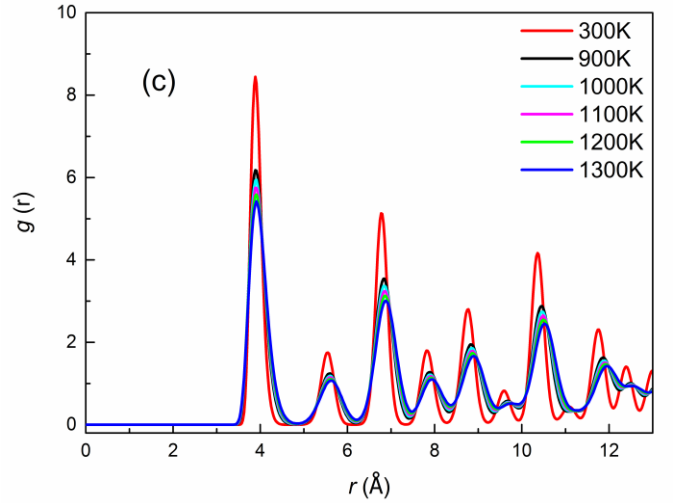


Fig 2 RDF curves of magnesium chloride:

(a)Mg-Mg; (b)Mg-Cl; (c)Cl-Cl.

3.2 Coordination number

As Fig.3 shows, it can be seen from the coordination number curve that the coordination number of each particle pair remains substantially unchanged with the increase of temperature. The coordination number of Mg-Cl is approximately 4, and it is the smallest among the three coordination numbers, indicating that in the molten salt structure.

Mg^{2+} and Cl^- will form a tetrahedral structure with a relatively close distance. The distance between Mg^{2+} and Mg^{2+} is larger because Mg^{2+} is at the center of a small group of each tetrahedral structure, so the distance between different centers is obviously larger.

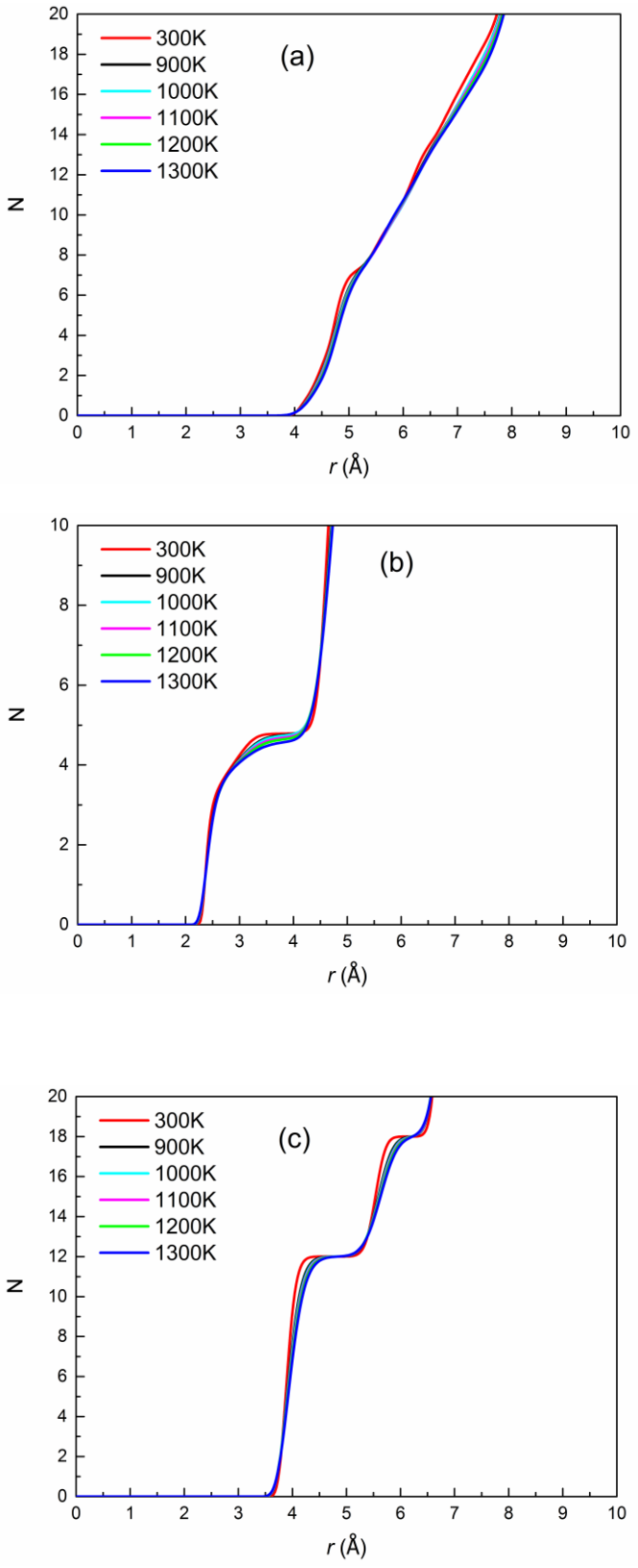


Fig 3 CN curves of magnesium chloride:

(a)Mg-Mg; (b)Mg-Cl; (c)Cl-Cl.

3.3 Density

The simulation results of magnesium chloride molten salt were calculated, and the density calculation results at each temperature and the density experimental measurements based on the Archimedes test principle were obtained [7].

It can be seen from the graph that the density simulation result of $MgCl_2$ molten salt is too large, and the relative error between the simulation result and the experimental value at 1100K is 9%. At the same time, the molten salt of $MgCl_2$ decreases linearly with increasing temperature, which is consistent with the trend of experimental measurements. In the $MgCl_2$ melt, the distance between $MgCl_2$ particles increases with temperature, and the melt volume follows. It becomes larger, so that the molten salt density decreases as the temperature increases.

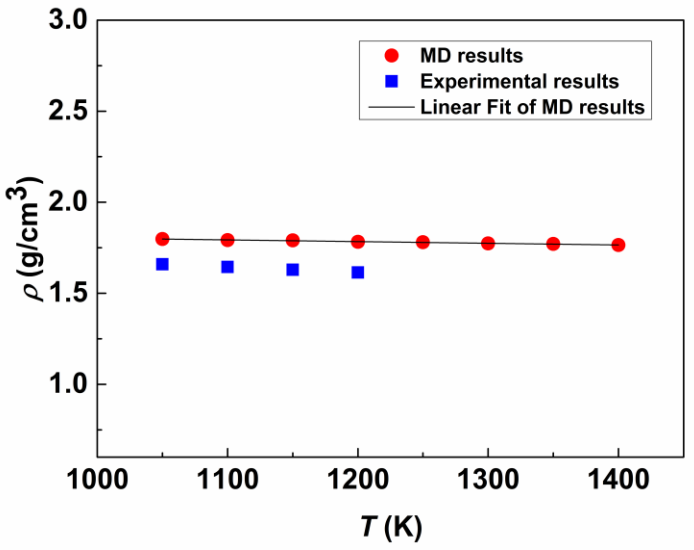


Fig 4 Density results of magnesium chloride

3.4 Thermal expansion coefficient

The simulation results of the molten salt of magnesium chloride were calculated, and the thermal expansion coefficients of the molten salt of $MgCl_2$ at each temperature were as shown in the following figure.

It can be seen from the figure that the coefficient of thermal expansion of $MgCl_2$ molten salt increases linearly with increasing temperature, because in the $MgCl_2$ melt, the distance between $MgCl_2$ particles

becomes larger as the temperature increases, and the melt volume becomes larger. Thereby, the coefficient of thermal expansion of the molten salt increases as the temperature increases. As the temperature rises, the coefficient of thermal expansion increases, and the volume of the melt increases, causing the density to decrease with increasing temperature.

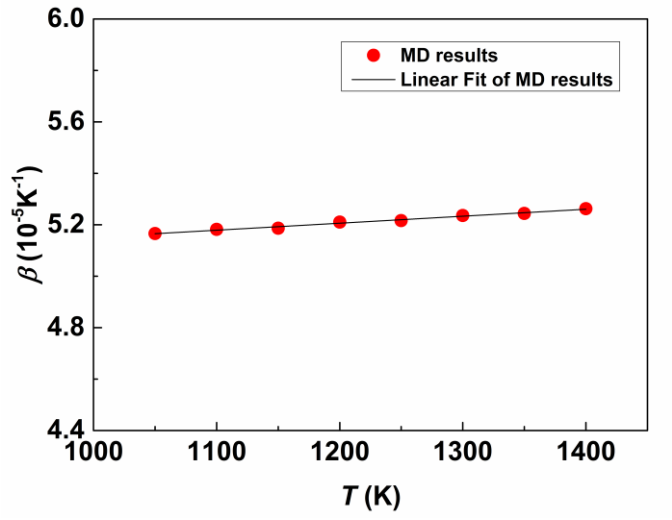


Fig 5 Thermal expansion coefficient results of magnesium chloride

3.5 Thermal Conductivity

In this paper, the thermal conductivity of MgCl2 molten salt is calculated by EMD simulation method.The relative error between the simulation calculation of the thermal conductivity and the experimental value [8] using molecular equilibrium dynamics (EMD) is only 0.84%.

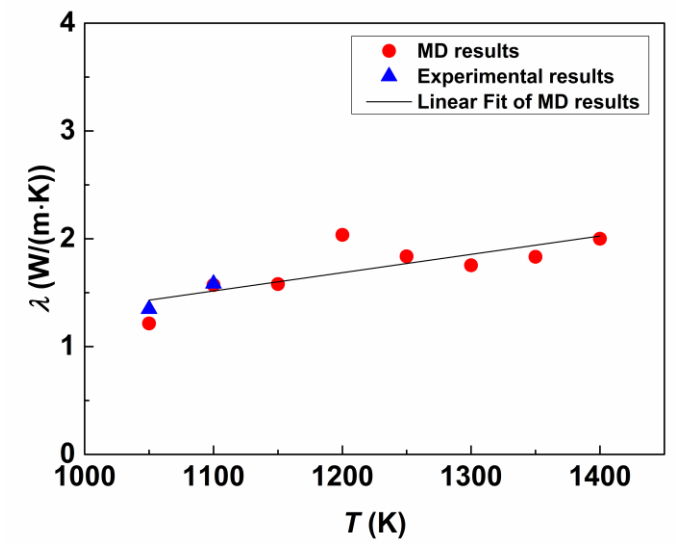


Fig 6 Thermal conductivity results of magnesium chloride

3.6 Specific heat capacity

Figure 7 shows the molecular dynamics simulation results of the specific heat of $MgCl_2$ molten salt. As can be seen from the figure, the specific enthalpy of the molten salt of $MgCl_2$ increases linearly with increasing temperature, and the slope, that is, the specific heat of the molten salt of $MgCl_2$, is 0.59 J/(g • K).

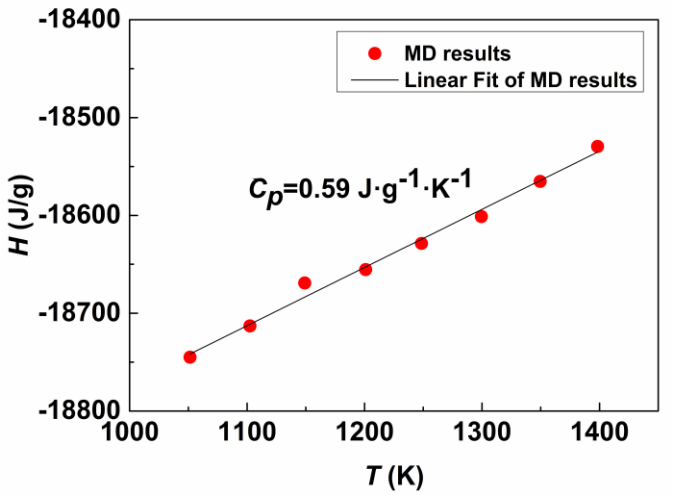


Fig 7 Specific heat capacity results of magnesium chloride

4. CONCLUSION

In this paper, thermal properties and microstructures of magnesium chloride were well predicted with MD method. The properties are calculated in a wide temperature range. The results show that Mg and Cl form the typical tetrahedral structure. As the temperature increases, RDF peak heights become smaller, density of magnesium chloride decreases. In addition, thermal expansion coefficient and thermal conductivity increase with increasing temperature. The deviations are so small that the MD results are reliable. This study helps to build the molten salt database for the application in industrial applications.

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REFERENCE

[1] Du LC, Xie WJ, Ding J, Lu JF, Wei XL, Wang WL. Molecular dynamics simulations of the thermodynamic properties and local structures on molten alkali carbonate Na2CO3. Int. J. Heat. Mass. Tran., 2019, 131: 41-51.

[2] Xie WJ, Ding J, Wei XL, Xia GF, Xing JT. Corrosion resistance of stainless steel and pure metal in ternary molten nitrate for thermal energy storage. Energy Procedia, 2019, 158: 4897-4902.

[3]Serrano-López R, Fradera J , Cuesta-López S.. Molten salts database for energy applications. Chemical Engineering and Processing: Process Intensification, 2013, 73:87-102.

[4]Xu XK, Wang XX, Li PW, Li YY, Hao Q, Xiao B, Elsentriecy H, Gervasio D. Experimental test of properties of KCl－MgCl2 eutectic molten salt for heat transfer and thermal storage fluid in concentrated solar power systems. J. Sol. Energ., 2018, 140.

[5]Wei XL, Song M, Wang WL, Ding J, Yang JP. Design and thermal properties of a novel ternary chloride eutectics for high-temperature solar energy storage. Appl. Energ., 2015, 156: 306-310.

[6]Li YY, Xu XK, Wang XX, Li PW, Hao Q, Xiao B. Survey and evaluation of equations for thermophysical properties of binary/ternary eutectic salts from NaCl, KCl, MgCl2, CaCl2, ZnCl2 for heat transfer and thermal storage fluids in CSP. Sol. Energ., 2017,152: 57-79.

[7]Bockris JO , Pilla A , Barton JL . Densities of solid salts at elevated temperatures and molar volume change on fusion. J. Phys. Chem., 1960, 64: 507-508.

[8]Bystrai GP, Desyatnik VN, Zlakazov VA. Thermal conductivity of molten mixtures of uranium tetrachloride with sodium and potassium chlorides. Soviet Atomic Energy, 1974, 36:654-655.